the same unsaturated residue— $C_6H_2Br_2O$ —which results from the catalytic decomposition of the silver salts of tribromophenol.

3. The compound obtained by Kastle and Loevenhart by the action of sunlight on tetrabromo-cyclo-hexadienone in carbon disulfide, is certainly poly-dibromo-phenylene oxide, again resulting from the loss of 2 atoms of bromine per molecule.

4. The action of tribromophenol bromide on silver tribromophenolate in chloroform does not give Benedikt's "hexabromo-diphenoquinone" as stated by Kastle and Loevenhart. Instead, the silver salt is catalytically decomposed by bromine resulting from the slow spontaneous decomposition of the tetrabromo-cyclo-hexadienone, which is otherwise unaffected.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

A CATALYTIC DECOMPOSITION OF CERTAIN PHENOL SILVER SALTS. IV. THE CONSTITUTION OF THE AMORPHOUS OXIDES.¹

BY W. H. HUNTER AND G. H. WOOLLETT.

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In previous communications from this laboratory it has been shown that silver salts of symmetrically tri-halogenated phenols can be decomposed smoothly into silver halide and colorless amorphous compounds of high molecular weight, by the catalytic action of undiluted ethyl iodide,² or of small amounts of iodine.³

It has also been shown² that the amorphous bodies formed have exactly the same composition of the silver salt, minus silver halide; in other words, they are polymerization products of the residue $C_6H_2X_2O$, which results when silver halide is eliminated. On this account, it has been suggested, that they be called poly-dihalogen-phenylene oxides.

Furthermore, it has been shown⁴ that the halogen may be removed either from the *para*- or the *ortho*-position, so that from any sample of salt, residues are formed, some of which, before polymerization, have the

¹ The work described in this paper formed part of a thesis presented to the Faculty of the Graduate School of the University of Minnesota by Guy Haines Woollett in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² THIS JOURNAL, 38, 1761 (1916).

³ *Ibid.*, 38, 2474 (1916).

⁴ *Ibid.*, 39, 2640 (1917).

Since all the oxides obtained at first were colorless, the assumption was made that they were formed in the simplest possible manner, by the coupling of large (and probably varying) numbers of these residues, carbon to oxygen, forming a succession of ether ties. It was presumed that this would result in the formation of various large cycles of benzene rings, united by oxygens.

An observation made in 1916, and reported by the junior author in a preliminary paper,¹ showed that from the silver salt of tri-iodophenol, 2 isomeric oxides could be obtained, a colorless one and a deep reddish-purple one, both of high molecular weight. The colorless one was obtained from the silver salt in the usual way, by the action of ethyl iodide, and also by the action of a trace of iodine in dry benzene. The colored one was always formed by the action of a minute amount of iodine in water.

This observation was a source of much satisfaction, as a substance of composition entirely analogous to that of our oxides, and of much interest on account of being a reddish-purple, had been obtained by Lautemann,² by the action of boiling alkali and iodine on salicylic acid, and later by Kammerer and Benzinger,³ by the action of potassium tri-iodide solution on a boiling solution of phenol in sodium carbonate.

Lautemann had ascribed to it the mononuclear formula

and called it di-iodo-phenylene oxide. Kammerer and Benzinger, however, decided that it was a diphenyl derivative, and named it tetra-iodo-

diphenyl quinone,⁴ $O = \text{C}_6\text{H}_2\text{I}_2 = \text{C}_6\text{H}_2\text{I}_2 = O$.

Much later, Messinger and Vortmann⁵ called it di-iodo-phenyl-hypoiodite, and ascribed to it the formula but apparently their

formula has not met with favor, as late references always use the diphenyl

¹ *Loc. cit.*

² Lautemann, *Ann.*, 120, 309 (1861).

³ Kammerer and Benzinger, *Ber.*, 2, 557 (1878).

⁴ It is interesting to note that they were undoubtedly greatly influenced by the fact that just before their publication, A. W. Hofmann (*ibid.*, 2, 333 (1878)) had shown that cedrret (or coerulignone) could be obtained from *s* pyrogallol dimethyl ether, by oxidation, and cedrret had not long before been shown by Liebermann (*Ann.*, 169, 221 (1873)) to be tetramethoxy-diphenoquinone.

⁵ Messinger and Vortmann, *Ber.*, 23, 2733 (1890).

formula. Investigation of their method indicates that they had in hand principally tri-iodo-phenol, with a large impurity of Lautemann's oxide.¹

Identity of Products.

Samples of this substance, which we will call "Lautemann's Red," until our view of its constitution is developed, were made according to the method of Lautemann, and also according to that of Kammerer and Benzinger. The very fact that one was made by alkali and iodine on salicylic acid, and the other by alkali and iodine on phenol, and that the iodine content agreed in each case, would seem sufficient evidence for assuming their identity. Kammerer and Benzinger had already made this assumption.

Since our substance also agreed in iodine content, and was made from the silver salt of tri-iodophenol, by the action of very small amounts of iodine, it was easy to assume further than our substance was the same as that obtained by the earlier workers. The one discrepancy was that Kammerer and Benzinger claimed to have "crystallized" their substance repeatedly from carbon disulfide, while we were unable to obtain crystals from any of the samples made by any method. We did, however, succeed in obtaining from carbon disulfide varnishes which cracked up, and gave fragments ("plate crystals") which were mistaken for crystals by many persons to whom they were shown. It is believed that this is the most probable explanation of the statements of Kammerer and Benzinger, as all samples made by all 3 methods agreed in the following properties.

Color: reddish, varying from deep pink to reddish-purple.

Calc. for $(C_6H_2I_3O)_n$: I, 73.82. Found by Lautemann, I, 73.70;² found by Kammerer and Benzinger, 73.19,³ 73.43, 73.63; made by method of K. and B., 73.54, 73.25; from silver salt of tri-iodophenol, 73.28.⁴

To assure ourselves further, it was decided to make a pure sample of the potassium salt of tri-iodophenol and treat it with iodine, thus checking at the same time our reaction with the silver salt and the other methods, which obviously amount to the action of iodine on a solution of more or less pure sodium salt. A pure sample of potassium salt was finally obtained by making use of a modification of the procedure used by Atkins and Wilson for preparing anhydrous substances. On treatment of the salt with a minute amount of iodine in water, a sample of "Lautemann's Red" was obtained, in 94.7% yield. Two analyses of this gave 73.20 and 73.62% of iodine. It was found that exposure to light also produced "Lautemann's Red" from solutions of pure salt.

¹ It is noteworthy that Messinger and Vortman made no reference to the earlier work on the subject, and that they patented the method, although Kammerer and Benzinger had anticipated them by many years, even to the preparation of the thymol derivative called by them annidalin, and now well known as aristol.

² Lautemann, *loc. cit.*

³ Kammerer and Benzinger, *loc. cit.*

⁴ THIS JOURNAL, 38, 2477 (1916).

Molecular weights were next determined, with bromoform and ethylene dibromide as solvents.

Calc. for $C_6H_2I_2O$: Mol. wt. 344. Found: by method of K. and B. "Lautemann's Red," 4800 ($C_2H_4Br_2$), 2300 ($CHBr_3$), 2300 ($CHBr_3$), 3100 ($CHBr_3$); from potassium salt, 2800 ($CHBr_3$); from silver salt, 5100 ($C_2H_4Br_2$), 4100 ($C_2H_4Br_2$).

Quinoid Oxygen.

These determinations and direct comparison of appearance and physical properties made it certain that only one substance was concerned. Our attention was accordingly turned to the problem of the oxygen tie. It seemed most probable that the difference between the white and the red oxides from tri-iodophenol lay in the attachment of the oxygens. The presence of color led immediately to the idea that some of the residue $C_6H_2I_2O$ was in the quinoid form.

Since hydrazine reduces quinones readily, it was decided to use an alkaline solution of hydrazine sulfate, and measure the nitrogen evolved. With true quinones, 4 quinoid oxygen atoms set free a molecule of nitrogen, according to the equation

As we were not prepared to decide how the oxygen was tied in the red oxide, the same equation was used in our calculations, although the reduction of a carbonyl to a secondary alcohol group would of course use twice as much hydrazine for each oxygen.

Tests on cedriret and on tetrabromo-diphenoquinone showed that the method is very accurate. Cedriret gave 10.53% of quinoid oxygen, as against 10.57 calculated, and the tetrabromo-diphenoquinone gave 6.57 and 6.42% (calculated 6.40).

On examining the red oxide in this manner, we found that it contained very little quinoid oxygen. If it were the tetra-iodo-diphenoquinone, it should give 4.65%; but 3 determinations on a sample purified only by boiling in alcohol gave 0.36, 0.40, 0.75%, respectively.

Samples purified by solution in carbon disulfide and reprecipitation, gave (I) 0.75, 0.81, (II) 0.95, 0.91, (III) 0.41, (IV) 0.39, (V) 0.47. If the oxygen were reduced to a "secondary alcohol" stage, the actual per cents. would be $\frac{1}{2}$ those given.

The wide variation in quinoid oxygen content agrees with the variation in color observed, and is probably also connected with the variations observed in molecular weight.

Structure.

On the basis of the observations so far recorded, the following hypotheses were made as to the structure of "Lautemann's Red." It was decided that the colorless oxides usually resulting from these salts, were to be assumed to have the structure already indicated, a series of halogen-

substituted benzene rings, united by oxygen. The Lautemann's Red, it was decided, must be one of three things: (1) A mixture of the colorless poly-di-iodo-phenylene oxide with some of the true dinuclear quinone (tetra-iodo-diphenylene quinone); (2) a mixture of oxides containing residues of the 4 possible different types, united in different proportions in different ways, and in different numbers; (3) a mixture of the colorless poly-di-iodo-phenylene quinone with an oxide of Type 2.

Experiments to settle the first possibility were of 2 kinds. It was first attempted to isolate some of the tetra-iodo-diphenylene quinone from the mixture. All such attempts failed, no trace of a crystalline substance of any kind being found, after the removal of tri-iodophenol by alcohol, and no quinone being found in the alcohol extract.

The next step was the preparation of a synthetic mixture. No success attended our attempts to make the tetra-iodo-diphenol, so we were compelled to resort to an analogy. A sample of the pure potassium salt of tribromophenol was prepared, and on treatment with a little iodine in water, we obtained a light brownish-red substance, with the same bromine content as the colorless poly-dibromo-phenylene oxide. By fractional precipitation this was separated into a very slightly colored part and a brownish-orange substance. This, the bromine analogue of Lautemann's Red, was purified and mixed in many different proportions with pure tetrabromo-diphenquinone, in powder and by evaporation of combined solutions, but no difficulty was experienced in separating the 2 substances, no matter how they had been combined. The difference of solubility is very great, the tetrabromo-diphenquinone dissolving in chloroform at ordinary temperature only to the extent of 0.01%, while the brominated oxides are extremely soluble.

This showed to our satisfaction that the bromine analogue of Lautemann's Red was not a mixture of the tetrabromo-diphenquinone and the colorless poly-dibromo-phenylene oxide, and our failure to obtain any crystalline substance from the Lautemann's Red seems sufficient evidence that it does not contain any of the tetra-iodo-diphenylene quinone.

It seemed wise, however, to use further means to settle this point, so a large amount of Lautemann's Red was prepared by the action of potassium tri-iodide on an alkaline solution of phenol. It was carefully extracted with alcohol and then dissolved in carbon disulfide and precipitated by ligroin. This was called Stage A. A sample was analyzed for iodine and quinoid oxygen, and its molecular weight taken. The rest was put through the following cycle, each step being sampled, analyzed, and a molecular weight determination made.

Stage A was reduced by hydrazine sulfate in 1-1 potassium hydroxide solution, giving Stage B. This was acetylated by acetic anhydride and a little ferric chloride, giving Stage C. This was hydrolyzed by alco-

holic potash, to Stage D, which was dissolved in carbon disulfide. About 10% would not dissolve, but this interesting observation was not pursued. Part of the carbon disulfide solution was oxidized by lead peroxide giving a substance, Stage E, identical in appearance with the original Lautemann's Red. The analytical results are here tabulated.

Stage.	Color.	Iodine con- tent. %.	Quinoid oxy- gen. %.	M. wt.
A	Red (original)	73.54	0.36	4800
		73.25		
B	Colorless (reduced)	73.24	0.0	4500
				5000
C	Colorless (acetyl derivative)	72.19	0.0	4600
		71.88		4800
D	Colorless (hydrolyzed)	73.25	0.0	5400
E	Red (re-oxidized)	73.82	0.36	5500
		73.42		6400
				8500

If all oxygen quinoid ($C_6H_2I_2O$)₂..... 4.65

At every stage, care was taken to look for crystalline substances, such as should have resulted if any of the dimolecular quinone were present, but none were found.

It thus became evident that no tetra-iodo-diphenquinone was in the mixture. These experiments also show that the part of the oxygen in the molecule which is reduced by hydrazine, forms hydroxyl groups (in Stage B) which can be acetylated. Further, these acetyl groups can be saponified and hydroxyl groups reappear (in Stage D). Both Stage B and Stage D can be oxidized to a red substance, which was analyzed for the last stage. Stage C could not be so oxidized, as would be expected.

Since the amount of oxygen which can be thus reduced is small, it becomes evident that most of the oxygen is in ether ties, as in the white oxides. Since the molecular weight, the color, and the amount of quinoid oxygen all vary in different samples, it seems necessary to believe that the Lautemann's Red is a mixture of polymerization products containing

residues of the formula $= \text{C}_6\text{H}_2\text{I}_2 = \text{O}$, together with the more com-

mon residues $-\text{C}_6\text{H}_2\text{I}_2\text{O}-$ and $\text{I}-\text{C}_6\text{H}_2\text{I}_2-\text{O}-$. It is also possible that *ortho*-quinoid residues are formed to some extent, of the type

$\text{I}-\text{C}_6\text{H}_2\text{I}_2=\text{O}$. The variations in color, molecular weight, and quinoid

oxygen must simply reflect the conditions of formation of any given sample, which would decide the number of the different styles of residues which

will be formed, the speed with which they will unite, the manner of union, and the number which will tie together.

Fig. 1.

As a last piece of evidence for the existence of the quinoid residues photographs were taken of the visual and ultra-violet absorption spectra of the various substances. The accompanying curves (Fig. 1) show, first, the close analogy existing between the Lautemann's Red and its bromine analogue; second, the difference between these and the colorless bromo oxides; third, that the true diphenquinone gives a band in the visible,

analogous to that given by the colored oxides, but more persistent and with its head further toward the blue.

At first sight, this seems to make it probable that II, the bromine analogue of Lautemann's Red, actually contains some of I, the true diphenylene quinone. Aside from the fact that no crystalline compounds appeared in our work, reference to the curves shows that the heads of the bands, which can be directly compared, are in different places in I and II, but are almost indentially situated in II and IV. This seems to show that the band may be ascribed to the single quinoid ring. Its position in the spectrum would then be expected to vary from compound to compound, according to the constitution of the whole molecule.

All the evidence then points toward the Lautemann's Red and its bromine analogue being substances made up of varying numbers of different residues, partly benzenoid and partly quinoid. No evidence has been found which can decide whether or not some of the colorless oxide is present in each case, as in Hypothesis 3, since the solubilities are very similar, and the presence of benzenoid residues in the colored oxides would mask the effect in the spectra. The important thing for the research on the catalytic decompositions, is that the quinoid residues occur, and that more evidence is presented for the smooth formation of unsaturated residues from phenol salts.

It is obviously futile to attempt to write a constitutional formula. The variations in molecular weight, etc., the colloidal nature of the substances, lead us simply to view them as a sort of pile of residues, attaching themselves as best they may, in the time available for saturation of their bonds. Probably many different arrangements and molecular weights are represented in a given sample.

The only requirements are, that different kinds of residues must be present, and some of the oxygens must be present as quinoid carbonyls, which can be reduced, and acetylated, and then brought back to the original condition and composition. It is perhaps not even necessary to close up all the ties, as the work of Pummerer and Frankfurter¹ on oxidation of phenols gives evidence that in large molecules, an oxygen singly tied to a benzene ring may exist in solution, at least, without any other group being tied to it. This work, so important for the theory of our reaction, will be referred to again in later communications.

Nomenclature.

In order to distinguish the Lautemann's Red and its bromine analogue from the colorless isomers, it seems best to use the prefix *chromo-*. On this basis the "Lautemann's Red" should be called *chromo-polydi-iodophenyleneoxide*.

¹ Pummerer and Frankfurter, *Ber.*, **47**, 1472 (1914); **47**, 2957 (1914).